

EFFECT OF TEMPERATURE ON FUNCTIONALITY CHANGES DURING COAL LIQUEFACTION

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Keywords: Liquefaction, functional groups, FTIR analysis

INTRODUCTION

This paper discusses characterization of solids from the liquefaction of Black Thunder subbituminous coal using Wilsonville coal-derived solvents with and without dispersed molybdenum-containing catalyst precursors. The overall goals of the present investigation are to investigate low cost subbituminous coal liquefaction concepts using dispersed catalysts and to evaluate low temperature, short contact coal pretreatment to decompose carboxylic acids.

EXPERIMENTAL

A sample of Black Thunder subbituminous coal was used for the present investigation. The coal was pulverized under N_2 and screened to pass 100 mesh. The liquefaction solvents were coal-derived liquids obtained from the Wilsonville Advanced Coal Liquefaction Facility from runs made with Black Thunder subbituminous coal. Elemental analyses of the coal and solvent samples on a dry basis are given in Table I.

The liquefaction runs were made in a 300 cc, stirred tank single-stage continuous feed unit at temperatures of 316-449°C and space times of 14-30 minutes. The space time was calculated by dividing the reactor volume by the volumetric feed rate. The lower temperature runs (316 to 371°C) were carried out with Solvent A, a solvent blend consisting of 40 wt% ROSE®-SR resid and 60 wt% V-1074 vacuum bottoms (343-538°C). The higher temperature (399-449°C) runs were made Solvent B, which consisted of only V-1074 vacuum bottoms. Neither solvent had any THF insoluble materials to start with. After a line-out operating period, product slurry samples were extracted with tetrahydrofuran (THF). The residue was dried in a N_2 swept vacuum oven at -60°C. Coal conversion was calculated on a moisture-ash-free (MAF) basis as the difference between weights of the feed coal and THF insoluble residue.

Infrared Spectroscopic Analysis of Liquefaction Residues: The THF insoluble residues in KBr pellets were analyzed by quantitative FTIR spectra on a Mattson Cygnus 100 FTIR spectrometer with a MCT detector. Sample preparation and spectral acquisition were performed in an inert atmosphere to prevent moisture absorption and air oxidation of the sample. Transmission FTIR spectra were obtained at 4 cm^{-1} resolution using 1000 averaged scans. The following data manipulations were performed on the FTIR spectra: 1) mild smoothing to eliminate spectral fringing, 2) spectral subtraction of the H-bonded water spectrum to eliminate the absorbance band near 1630 cm^{-1} due to the bending vibration of water absorbed or chemically bound to the sample or KBr, 3) a baseline correction in the 1500-1750 cm^{-1} region that consisted of overlapped bands of carbonyl and aromatic functional groups, and 4) curve fitting (Curvefit in Spectra Calc Software of Galactic Industries) to fit spectra to individual line shapes (Gaussian/Lorentzian profile.)

All FTIR intensities were normalized to the weight of the starting coal sample, to reflect the concentration of each functional group present in the residue on a starting material basis. This method of weighting is only qualitative, because the soluble portion and the residue do not have the same distribution of functional groups.

RESULTS AND DISCUSSION

Coal Conversion. Coal conversion to THF solubles in the thermal and catalytic liquefaction runs is summarized in Figure 1. At 399 and 427°C catalyst addition caused 2 - 5% increase in the THF solubles. At 441 and 449°C this difference increased to ~8%. The THF insoluble fraction is considered to be "unconverted coal"; however, previously dissolved coal-derived components that have undergone retrogressive coking reactions also may become insoluble in THF.

Elemental Composition of THF Insolubles. The H/C and O/C ratios of the THF insolubles from both non-catalytic and catalytic runs are summarized in Table II. These results follow expected trends with increasing liquefaction temperature. The H/C ratios of the 316 and 329°C THF insolubles were marginally higher than that of the feed coal. This is presumably due to some incorporation of the solvent into the coal solids. With the start of liquefaction, the H/C ratio decreased with increasing temperature and coal conversion. The O/C ratio also decreased as temperature increased.

Petrographic Examination of Unconverted Coal. A visual separation of the unconverted coal from coke can be achieved by petrographic analysis. Selected results of the microscopic examination of samples of raw coal and THF insolubles are presented in III. In summary, the resinous liptinite was completely converted as reaction temperature increased, the vitrinite and semi-inertinite macerals were progressively converted, and the inertinite underwent little conversion and was concentrated in the THF insolubles. Vitroplast (coke) formation was high at 449°C.

FTIR Characterization of THF Insoluble Fractions. The functional groups that were studied included aliphatic C-H, carboxyls, and ethers. The weighted FTIR intensities of these functional groups were plotted on an arbitrary scale against liquefaction temperature in Figures 2-7. Hydroxyl groups were not analyzed because of the difficulty in quantifying the O-H stretching bands due to the interference from moisture.

Aliphatic C-H: For most organic compounds, the aliphatic C-H bond stretching bands can be found in the 2890-2970 cm^{-1} region^(1,2). Although the liquefaction residue is highly aromatic, the aromatic C-H bonds are less abundant than the aliphatic C-H bonds because of the preponderance of multinuclear aromatic structures present in the residue⁽²⁾. The weighted intensities of the absorption bands in the range of 2800-3000 cm^{-1} for non-catalytic and catalytic residues are plotted against reaction temperature in Figures 2 and 3, respectively. The data indicate that for the non-catalytic residue, the C-H intensity stays the same up to 371°C and then slowly decreases. For the catalytic residue, the C-H intensity of the residue increases after the liquefaction at 343°C and then decreases at a faster rate than the non-catalytic residue. Both catalytic and non-catalytic liquefaction at 449°C produces similar residues, indicating a maximum coal conversion at that temperature. It appears that the soluble catalyst assists hydrogenation at lower temperatures and dehydrogenation at higher temperatures. Therefore, attention should be given to the appropriate temperature range when selecting the most beneficial coal liquefaction catalysts.

Carboxylate Groups: The weighted intensities of aliphatic acids (1675-1725 cm^{-1}), aromatic acids (1645-1665 cm^{-1}), and carboxylate anions (1534-1560 cm^{-1}) in non-catalytic and catalytic residues are plotted against reaction temperature in Figures 4 and 5, respectively. These data indicate that the aliphatic acids decompose much more rapidly than the other two types, and the levels of decomposition in both the non-catalytic and catalytic runs are essentially the same. This observation is consistent with published data⁽²⁾. It is also known that the shorter the aliphatic chain, the faster the carboxyl group decarboxylates⁽³⁾. Therefore, it appears that Black Thunder coal may not contain significant quantities of long chain fatty acids.

While aliphatic acids begin to decarboxylate at lower temperatures, in the absence of a catalyst, aromatic acid content decreases significantly only above 399°C. It has been reported that thermally, aromatic acids decarboxylate easily if there are activating groups present on the aromatic ring.^(4,5) For example, a hydroxyl group in the *ortho* position can stabilize the carboxylate activated complex by hydrogen bonding and thus enhance the rate of decarboxylation. The results of the non-catalytic liquefaction runs indicate that the Black Thunder aromatic acids do not contain suitable activating groups for facile decarboxylation. However, the dispersed catalyst assists decarboxylation of the aromatic acids even at 343°C.

It appears that the carboxylate ions are virtually unaffected in the non-catalytic runs. However, in the presence of the catalyst, the carboxylate concentration decreases slowly with temperature and substantial decarboxylation occurs at 449°C.

In short, during non-catalytic liquefaction only the aliphatic acids decarboxylate significantly. In contrast, decarboxylation of all three carboxylate types are enhanced by the dispersed molybdenum catalyst.

Ether and Hydroxyl Groups: Identification of ether groups from the infrared spectra of complex organic molecules is notoriously difficult because the characteristic bands (1100-1300 cm^{-1}) of these groups appear in the midst of absorbance bands of many other groups, especially those of water and hydroxyl groups. (Because the samples were dried under nitrogen and the KBr pellets were handled in a dry atmosphere, the amount of moisture present in the test samples is assumed to be negligible compared to that of the hydroxyl groups.)

For this discussion, the absorption band centered at the 1100 cm^{-1} (1140-1065 cm^{-1}) is considered to be due to the ether groups, the bands in the range of 1065-1020 cm^{-1} (peaking at 1040 cm^{-1}) are assigned to both ethers and hydroxyls, and the bands in the range of 1020-990 cm^{-1} (peaking at 1010 cm^{-1}) are assigned to substituted furans - possibly dibenzofurans^(6,7) and to alcohols β to an aromatic ring^(7,8). Several layered silicates also have strong bands in this region^(9,10). However, because of the small amount of mineral matter present in the starting coal, the contribution from the silicates is not considered predominant.

The ether group intensities in the non-catalytic and catalytic residues are plotted against liquefaction temperature in Figures 6 and 7, respectively. For the non-catalytic runs, the ether band intensity at 1100 cm^{-1} increases with temperature above 343°C. This is a clear indication of the formation of ether bonds as the liquefaction severity is increased. Most likely the ether bonds are of diaryl type

and could be formed by condensation of phenolic groups with other phenolic groups or with aromatic structures. The diaryl ether bonds are thermally very stable, and their formation indicates significant retrogressive reactions during uncatalyzed coal liquefaction above 399°C.

The 1040 cm^{-1} band shows a slight increase in intensity in the residue from the 399°C reaction, but decreases with further increases in temperature. The high intensity of this band at lower temperatures is probably due to the formation of hydroxyl groups (alcohols or phenols) by the hydrolysis of ethers. These hydroxyl groups disappear by hydrogenation at higher temperatures and therefore, their intensities are reduced.

The ether and hydroxyl group intensities of the residues from the catalytic runs show a significantly different pattern from that of the residues from the non-catalytic runs. The changes in the 1100 cm^{-1} band intensity with temperature for the catalytic runs are much less marked than those for the non-catalytic runs. In contrast, the intensity of the ether band at 1040 cm^{-1} approximately doubled with a temperature increase from 316 to 343°C, and it subsequently decreased with increase in temperature, indicating substantially different reactions in the catalytic and non-catalytic runs. The overall effect of the catalyst is to reduce in the ether/hydroxyl group concentration in the residue.

The behavior of the 1010 cm^{-1} band also differs in the presence of the catalyst. The intensity of this band, which may be due mainly to dibenzofurans and hydroxyls β to an aromatic ring, increases significantly above 399°C. Above 399°C, the contribution to this band could be primarily from dibenzofurans. Since the curves for the 1040 cm^{-1} and the 1010 cm^{-1} band intersect slightly above 399°C, it is tempting to conclude that at this temperature, the hydroxyl groups may be effectively converted to the dibenzofurans in the presence of the catalyst. Quantitative measurement of hydroxyl and dibenzofuran groups is necessary to confirm this hypothesis.

CONCLUSIONS

The following conclusions are drawn from the characterization of THF insolubles generated from the liquefaction of Black Thunder subbituminous coal using a short contact time, single-stage, continuous flow reactor: Dispersed molybdenum catalyst precursor enhances the dissolution of coal to THF solubles by 3 to 8% depending upon reaction temperature. It assists hydrogenation at lower temperatures and dehydrogenation at higher temperatures. The addition of the catalyst also serves to decrease the level of ether/hydroxyl groups left in the residue.

Aliphatic acids decompose much more rapidly than the other types of acids, and the level of their decomposition is not influenced by the presence or absence of the catalyst. The aromatic acids and carboxylate ions do not undergo facile thermal decarboxylation. The dispersed molybdenum catalyst facilitates decarboxylation of all carboxylate groups.

A number of retrogressive reactions occur during coal liquefaction above 427°C. This is confirmed by the presence of a high concentrations level of vitroplast and dibenzofuran type structures in the THF insoluble residues.

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TABLE I
ELEMENTAL ANALYSES OF COAL AND SOLVENTS

	Coal	Solvent A	Solvent B
Elemental Analyses, Wt% (Dry basis)			
Carbon	69.60	89.56	87.23
Hydrogen	5.01	8.26	9.68
Nitrogen	1.07	0.80	0.53
Oxygen (diff)	17.14	1.33	2.52
Sulfur	0.46	0.05	0.04
Ash	6.72	0.0	0.0

TABLE II
CHANGES IN THE ATOMIC RATIOS OF LIQUEFACTION RESIDUE FROM
BLACK THUNDER COAL WITH TEMPERATURE

Temperature(C)	Conversion,wt%		H/C		O/C	
	n-c	c	n-c	c	n-c	c
316	4.8	-	0.85	-	0.17	-
329	9.3	-	0.84	-	0.17	-
343	6.5	16.5	0.81	0.91	0.14	0.21
357	16.5	-	0.80	-	0.15	-
371	24.2	35.8	0.79	0.89	0.14	0.19
399	52.5	57.9	0.79	0.87	0.17	0.18
427	63.1	73.3	0.77	0.87	0.15	0.18
441	72.9	-	0.74	-	0.11	-
449	72.9	81.2	0.68	0.77	0.09	0.14

n-c = non-catalytic; c = catalytic

TABLE III
PETROGRAPHIC ANALYSIS OF BLACK THUNDER COAL AND
LIQUEFACTION RESIDUES

	Coal	399°C Residue	449°C Residue
THF Insolubles, wt%	99	42	19
Maceral Distribution, wt%			
Huminite(vitrinite)	82	78	39
Liptinite	3	1	0
Semi-inertinite	7	6	8
Inertinite	5	10	26
Vitroplast	3	5	27

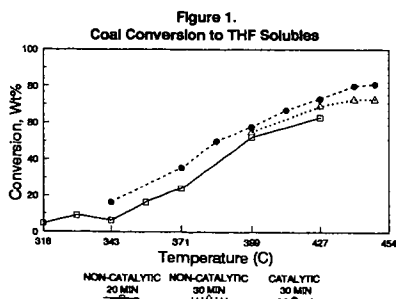


Figure 2.

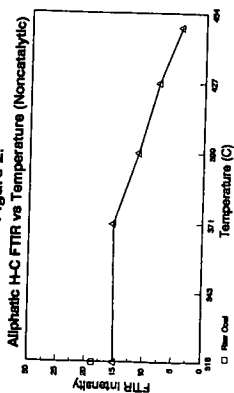


Figure 4

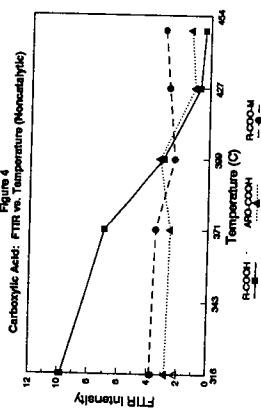


Figure 3.

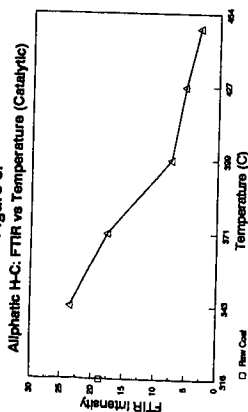


Figure 5

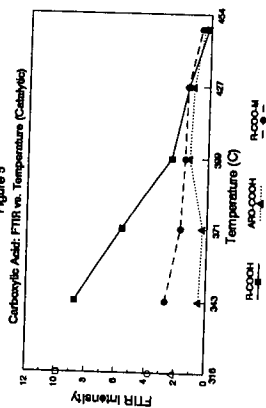


Figure 6

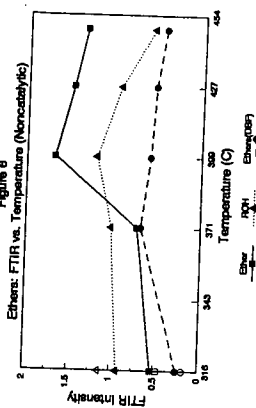


Figure 7

